

THE THERMAL DECOMPOSITION OF SODIUM BETA"-ALUMINA SOLID ELECTROLYTE CERAMIC

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ABSTRACT

Sodium beta"-alumina is one of the best characterized solid electrolytes, but its high temperature chemistry in the range 700K to 1800K is only partly understood. In particular, the kinetics of slow degradation reactions of sodium beta"-alumina have not been definitively characterized. We have begun investigation of high temperature processes in the range 1000K to 1500K which may lead to degradation of sodium beta"-alumina in alkali metal thermal to electric converter (AMTEC) devices. AMTECs are under development as power sources for future outer planetary robotic space missions, where they must operate for very long times. Mission duration and high temperature operation of AMTECs, to perhaps 1250K, have driven the need to investigate potential degradation reactions at even higher temperatures to greatly accelerate testing.

Modeling predicted very slow and highly activated loss of sodium oxide into a gas phase comprised of low to moderate pressure sodium gas and extremely low pressure oxygen at typical AMTEC operating conditions. Experiment has provided some conformation for this prediction. Sodium oxide loss is strongly thermally activated and strongly suppressed by sodium gas pressure.

Faster thermal degradation by several evaporated transition metals on beta"-alumina yielding sodium gas is thermodynamically possible. Experiment shows that Cr and Mn lead to formation of $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ and MnAl_2O_4 after hundreds of hours at 1273K to 1373K, but reaction with Fe is much slower or negligible under these condition. Experiment also indicates that sodium oxide loss from beta" alumina into low oxygen activity liquid sodium does not occur at a significant rate at 1173 K. Under the same conditions, decomposition of 99.8% alpha Al_2O_3 to form NaAlO_2 is fairly rapid. These results allow utilization of appropriate liquid-fed as well as vapor-fed cell designs and may significantly influence materials selection and use of getters.

INTRODUCTION

AMTEC cells have been considered an attractive power source for a variety of long term robotic NASA missions. Long life models for AMTEC operation are therefore important.

If loss of oxygen from the solid electrolyte is sufficiently slow, getters such as Zr and Hf may be employed to scavenge trace oxygen and allow much greater flexibility in fabrication materials, since most metals are more rapidly attacked in liquid sodium containing significant sodium

oxide, compared with very pure liquid sodium.[1,2]

This paper presents observed rates and temperature dependence of sodium oxide loss from sodium beta"-alumina solid electrolyte (BASE) in vacuum at 1273 to 1473K, and on the observed time dependence of the solid electrolyte conductivity in low sodium vapor pressure sodium exposure test cells, at 1100 K and 1223 K. Additionally it presents experimental data on the high temperature attack of oxygen-free liquid sodium on both BASE and alpha alumina, and on the rates of high temperature attack of several transition metals on BASE in vacuum.

It is evident that both sodium beta-alumina and sodium beta"-alumina are thermodynamically stable phases at appropriate activities of sodium and oxygen. [3-14] Some uncertainty in the values of the free energies of formation of these phases remains, as does a quantitative understanding of the effect of spinel block stabilizing ions on the thermodynamic stability of the beta" and beta phases. The beta"-alumina phase is stabilized by spinel block stabilizing ions such as Li^+ and Mg^{2+} . The importance of stabilizing ions is suggested by the fact that the isostructural potassium beta"-alumina phase may only be thermodynamically stable when they are present, and may only be prepared by direct synthesis from constituent oxides if stabilizing ions are present. We will refer to the K-BASE phase as an analogous phase with more facile reaction kinetics. Sodium beta"-alumina may be thermodynamically stable without other ions in the spinel block

Stabilizing ions such as Li^+ and Mg^{2+} do confer greater stability, and seem to be necessary for the high temperature processing which yields pure, dense BASE ceramics. Phase studies indicate that pure sodium beta" alumina is not formed without stabilizing ions. [14] Our investigation utilized lithium stabilized beta"-alumina ceramic from Ceramtec (Utah) and from Ionotec (Britain).

We are interested in the thermal decomposition of BASE at $1000\text{K} < T < 1500\text{K}$ in vacuum and at low sodium gas pressures, in interactions of BASE

with liquid sodium or high pressure sodium gas, and also in decomposition induced by reaction with metal vapor or other contaminants in operating AMTEC cells under these conditions. It is critically important to the performance of AMTEC devices that the beta"-alumina solid electrolyte not suffer a major loss of ionic conductivity near its surface. It would be tolerable if some of the beta"-alumina phase were converted to the beta phase near the surface, since the beta phase is still a good ionic conductor, but device failure would occur if there were conversion of beta"-alumina to alpha alumina through loss of all sodium oxide at the surface. Both failure due to alpha alumina formation and the performance degradation due to moderate conductivity decrease must be incorporated into the AMTEC life model.

The phase diagram for the Na-Al-O system under reducing conditions has been evaluated and the calculated equilibrium vapor pressure of O_2 is very low.[8] Calculations of alkali oxide loss, as alkali gas and molecular oxygen have indicated that the alkali oxide loss reaction in operating AMTEC cells is slow below about 1100K. [15-18] This approach does not consider additional rate limitations imposed by chemical reaction kinetics, and gives a maximum value for the rate. Experiments reported here indicate that the process is more kinetically inhibited. The lowest previously reported temperatures for conversion between sodium beta alumina, sodium beta"-alumina and alpha alumina ceramics are typically at least 1600K in BASE and 1450K in K-BASE with reaction times of hours, but reported results are somewhat contradictory. [9-12, 19-23] No observation of alkali oxide loss in operating AMTECs has been described.

Because thermal decomposition of BASE produces $\text{Na}_{(g)}$ and O_2 simultaneously, O_2 loss is inhibited by sodium activity and is therefore strongly dependent on the AMTEC cell's discharge current. However in the limit of small cell discharge currents, sodium pressure due to shunt currents and the sodium vapor pressure at the condenser will dominate, so that eliminating the measured AMTEC discharge current will not lead to immediate rapid O_2 loss from the solid

electrolyte. The loss of oxygen from free Na_2O or from beta"-alumina with no crystallographic phase change or with a phase change to beta alumina would all be strongly activated, but may have a lower activation energy than conversion of BASE to alpha Al_2O_3 and Na and O_2 .

Kinetics of change in conductivity of BASE and K-BASE in high temperature low pressure sodium or potassium vapor show a brief decrease in conductivity, followed by a longer period in which conductivity does not change. [19] We found the amount of K-beta-alumina, initially present at about 1-2% in K-BASE, increased to about 3-4% after 500 hours at 1200K in about 2-3 Pa potassium vapor. [19] K-BASE thermal decomposition may be a kinetically faster or thermodynamically more facile model for degradation of the BASE phase. However, it could not be determined if the K-beta-alumina phase was formed from the beta"-alumina phase or from amorphous material, and the conversion appeared to complete in the first 100 hours of the experiment based on the conductivity decrease of about 20%, suggesting the reaction was limited to grain boundary regions and conversion of perhaps amorphous KAlO_2 . At 1123K, BASE shows a very small reduction (about 5%) in its conductivity during the first hundred hours, but no further degradation to about 1000 hours, and XRD indicates no production of a new phase.

The reverse reaction, by which alpha alumina is attacked by sodium or potassium gas at moderate activity to form beta (and beta"-) alumina has been characterized at lower temperatures, $T < 973\text{K}$, much more thoroughly than the disproportionation reaction of beta alumina. The alumina/alkali metal reaction has been addressed to the point of a general consensus among researchers in the field. While the disproportionation reaction should not proceed under the same conditions where the alkali metal attack on alpha alumina occurs, little information on either reaction at very low alkali metal pressure exists.

EXPERIMENTS

Sodium beta" alumina was heated in vacuum,

10^{-7} to 10^{-6} torr, for times up to 500 hours, in alpha alumina tubes, at temperatures above 1273K. BASE stability in low pressure (1-10 Pa) sodium atmosphere was also tested by measuring the electrolyte resistance of BASE in a four probe configuration during sodium exposure test cell operation at 1100K and 1223K for 900 and 500 hours respectively.

BASE samples were heated close to, but not in direct contact with, small pieces of Cr, Mn, or Fe metal, under similar conditions.

BASE ceramics and dense 99.8% alpha Al_2O_3 ceramics were heated in stainless steel capsules about 90% filled with sodium and zirconium getters at 1073K and 1173K for up to 500 hours, and were then opened in an argon filled glove box and analyzed by scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), and x-ray diffraction (XRD). Samples were analyzed by XRD, SEM and EDS to characterize the morphology, composition, crystal structure, and thickness of alteration layers formed near the samples surface.

RESULTS AND DISCUSSION

Transformation of sodium beta"-alumina into alpha alumina due to sodium oxide loss at 1373K, 1398K and 1423K in vacuum for times up to 500 hours is observed. Similar degradation to produce a new phase could not be observed after 500 hours at 1273K in vacuum, by XRD. The degradation reaction kinetics are complex; at 1373K and 1398K the reaction goes more slowly than at 1423K, and the amount of sodium oxide lost from the degradation layer is significantly less. There is some structure to the degradation layer. At 1373K and 1398K a zone of increased fracture and more defined grain boundaries extends further into the ceramic than the thin zone in which substantial Na_2O loss occurs. The depths of the primary degradation zone and the fracture zone which were measured at the three temperatures are shown vs. time at high temperature in Figure 1. At 1423K, the zone of substantial sodium loss contains a high contrast region of perhaps highly fractured or mechanically weakened material near to

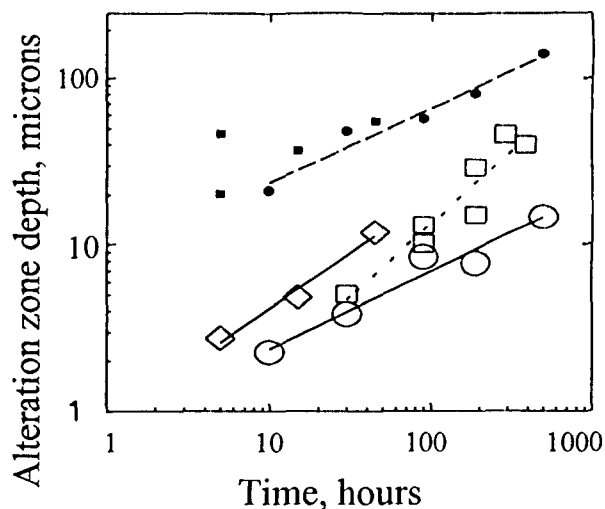


Figure 1: Depth of alteration layers in BASE vs. time at elevated temperature. ○ High Contrast Zone, 1373K; ● Fracture Zone, 1373K; ◇ High Contrast Zone, 1398K; ■ Fracture Zone, 1398K; □ 1423K.

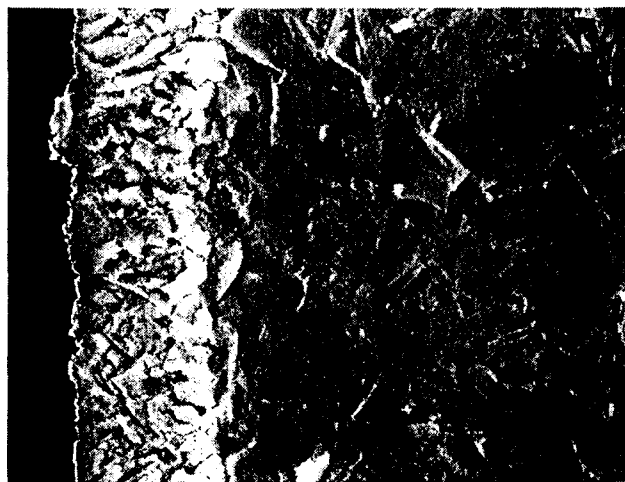


Figure 2: Degradation layer (to left) on BASE fracture cross section, after 290 hours at 1423K in vacuum. 500X

unaltered BASE, a porous region behind that, and a region in which porosity has decreased due to sintering of the altered material at the surface of the ceramic. A photomicrograph of a fresh fracture cross section across a BASE sample annealed 290 hours in vacuum at 1423K is shown in Figure 2, with the exposed surface to the left. Profiles of the oxygen to sodium ratio in samples annealed 90, 190, and 290 hours at 1423 are shown in Figure 3. Because the degradation to $\alpha\text{-Al}_2\text{O}_3$ is slower or more greatly activated

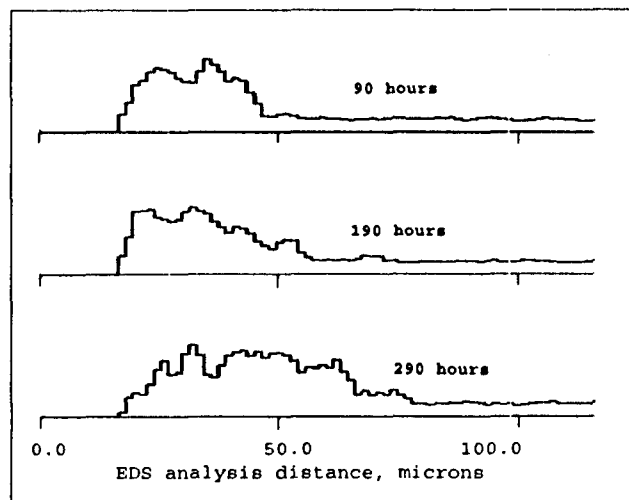


Figure 3: Relative oxygen to sodium ratio vs. distance perpendicular to edge on fracture cross sections of BASE samples annealed in 10^{-6} to 10^{-7} torr at 1423K.

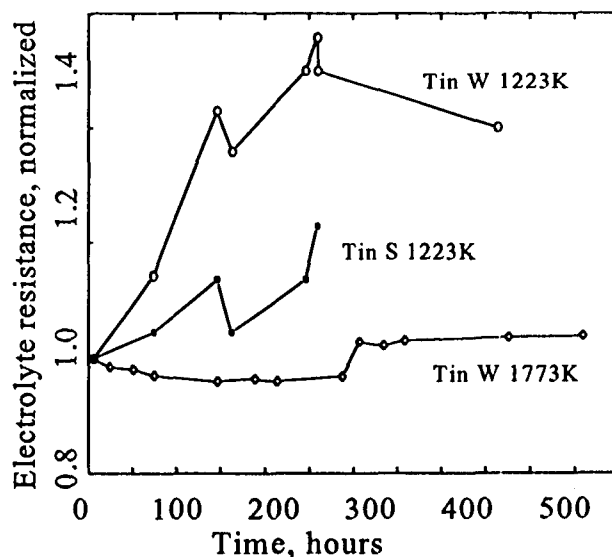


Figure 4: Electrolyte resistance between two inner TiN electrodes, measured in four probe configuration, for two groups of electrodes at 1223K and one group at 1173K. S=Sputter, W=Weber.

than predicted by the model based on thermodynamics and the kinetic theory of gases, the reaction probably has a substantial kinetics limitation associated with the initial bond breaking steps.

Conductivity tests in the SETC are described more completely elsewhere. In these tests, the

reported BASE conductivity, shown in Figure 4, was calculated from the estimated high frequency intercept of four probe impedance spectra measured at zero volts.

The test of ceramics in liquid sodium was somewhat unique in that the use of zirconium getters should have established an extremely low oxygen activity in the capsule shortly after it was taken to high temperature. Therefore both sodium reduction of the alpha Al_2O_3 and sodium oxide abstraction from the BASE might be potential reactions depending on the reaction kinetics.

The conversion of the alpha Al_2O_3 to NaAlO_2 was complete for a sample 2mm thick in its thinnest dimension, after exposure at 1123K for 500 hours. Some elemental aluminum was also found in the interior of the sample by use of XRD. The ceramic sample was highly distorted, expanded, and cracked at its surface, but was in one piece on removal from the capsule.

The BASE sample was dimensionally unchanged but discolored to a gray to black appearance. The dark color was probably due to neutral sodium color centers often observed in AMTEC tests, and exposure to atmosphere led to formation of some sodium salt deposits on the surface. Annealing at 1073K for an hour reduced the darkness of the ceramic and made it possible to handle it in air without surface deposits. This sample was unchanged BASE by XRD.

Metal vapor deposition on beta"-alumina leads to beta"-alumina decomposition, or possibly to relatively harmless reactions, or no reaction, depending on the metal and the conditions. The rate may be limited by deposition rate, activation energy, and high sodium activity, and will not be important for refractory metals or ferrous metals at sufficiently low temperature where their evaporation rate is negligible.

Reactive metal induced decomposition of BASE occurs more easily than thermal decomposition of BASE because no O_2 gas is formed; this should especially be true in sodium atmosphere. [20] Cr, Mn, Fe, and Co are all potential reactants according to JANAF thermochemical data. [21]

Free energies of attack by these metals on Na_2O at 1200K are shown in Table 1, along with the sodium pressures above which the degradation reactions are inhibited. The Na_2O constituent in BASE is somewhat, more stable than crystalline Na_2O . Only Cr and Mn reaction products were identified in this study. Chromium evaporated onto BASE at 1273 and 1373K in vacuum produces corundum structure (alpha alumina) phases, Cr_2O_3 and Al_2O_3 . The Cr reaction is confined near the surface in the top ten or so microns. Manganese evaporated onto BASE at 1373K in vacuum produces MnAl_2O_4 , a spinel phase. At 1273K Mn uptake by the ceramic was observed. Slight amounts of the spinel product may form at 1273K. Both Mn and Fe penetrate farther into BASE than Cr. Iron was detected within the outside 10-20 microns of the BASE surface at 1273K but no new reaction product phase is seen by XRD.

These reactions may proceed fairly rapidly once the highly activated step of metal atom volatilization has occurred, but the observed reaction rate must be compared with the expected arrival rate of metal atoms to determine if additional activation is required. Additional activation may be required for reaction once the metal atoms are deposited, and the decomposition reaction is more thermochemically favored at higher temperatures and lower sodium activities. However, as seen in Table I, these reactions may go at quite high sodium vapor pressures, and in the case of chromium, reaction is expected in saturated sodium vapor.

CONCLUSIONS

The stability of BASE with respect to thermal decomposition in vacuum suggests that the reaction has a significant activation energy above the free energy difference of reactant-to-products which inhibits the reaction. Therefore application of BASE in AMTECs at temperatures significantly below 1273K will probably not result in failure due to strictly thermal decomposition to alpha alumina at the BASE surface. Loss of a small amount of sodium oxide from BASE with either no phase change or very slow formation of the beta-alumina phase from

Reaction with all phases in standard states	Free Energy at 1200K	Equilibrium P(Na(gas))
$2\text{Cr} + 3\text{Na}_2\text{O} = \text{Cr}_2\text{O}_3 + 6\text{Na(g)}$	-92.709 kJ/mole	proceeds at 1 bar
$2\text{Mn} + 3\text{Na}_2\text{O} = \text{Mn}_2\text{O}_3 + 6\text{Na(g)}$	+75.815 kJ/mole	0.28 bar
$2\text{Fe} + 3\text{Na}_2\text{O} = \text{Fe}_2\text{O}_3 + 6\text{Na(g)}$	+213.392 kJ/mole	0.028 bar
$\text{Fe} + \text{Na}_2\text{O} = \text{FeO} + 2\text{Na(g)}$	+47.606 kJ/mole	0.10 bar
$\text{Co} + \text{Na}_2\text{O} = \text{CoO} + 2\text{Na(g)}$	+92.559 kJ/mole	0.010 bar

Table I: Thermodynamics of reaction rates related to decomposition of BASE.

the more conducting beta" alumina phase, or from sodium aluminate at grain boundaries, may still be possible and result in a small decrease in conductivity on initial operation at high temperature. We have not seen evidence of a sustained conductivity decrease, in tests at 1073K to 1223K in exposure test cell experiments of hundreds to thousands of hours. Conductivity tests and weight loss tests at temperatures below 1373K should provide more information about sodium oxide loss without alpha alumina formation.

The stability of BASE in low oxygen sodium and concurrent formation of NaAlO_2 from alpha alumina suggest that, under these conditions there is either (1) a difficult kinetic step to interconversion of BASE and NaAlO_2 , or (2) BASE with spinel block stabilization due to Li^+ (or Mg^{2+}) is a more stable phase than NaAlO_2 but that BASE without stabilizing ions is less stable than NaAlO_2 .

The degradation of BASE due to transition metal deposition at temperatures above 1273K indicates that these processes could pose a serious problem for AMTECs with hot side materials which can liberate volatile metals, especially Cr and Mn. Further tests with the metal source at higher

temperature than the BASE sample would be useful in determining if the metal evaporation or reaction kinetics of the metal atom on BASE is the rate determining step. Results of such tests would have implications for longer lifetime applications of these transition metals at lower temperature. Further acceleration of tests with Fe, Co, and Ni would also be useful as these appear more innocuous than Cr or Mn and may be used as constituents of structural alloys free of Cr and Mn.

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